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(54) **Resin composition comprising organoclays of improved dispersibility.**

(57) Resin-coating compositions, e.g. unsaturated polyester or epoxy resin compositions, are prepared using an organoclay of improved dispersibility. The organoclay is prepared by suspending a smectite clay in water to form a fluid suspension; treating the suspension with a solution of an inorganic salt, the cation of which has a valency of at least two, the concentration of the salt being such as to flocculate the smectite clay substantially completely; mixing the suspension of the flocculated smectite clay with a quaternary ammonium compound, at least one of the four alkyl groups of which has from 10 to 24 carbon atoms; and dewatering the resultant product.

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Resin Composition Comprising Organoclays of Improved Dispersibility

Field of the Invention

This invention relates to organoclays of improved dispersibility in organic media and to their applications in resin compositions, particularly for coating and forming purposes.

Background of the Invention

10 An organoclay is an organophilic cation-modified clay derived from a clay mineral, generally of the smectite group, for example a bentonite, montmorillonite, hectorite, saponite or the like, by replacing the inorganic exchangeable cations, which occur in the natural clay mineral, by organic cations, each comprising at least one hydrocarbon radical which has sufficient carbon atoms to render the surface of the cation-exchanged clay hydrophobic.

15 Organoclays have been found to be very useful as thixotropic agents in organic media such as, for example, lubricating greases, oil-based drilling fluids, paints, varnishes, enamels and printing inks. However, an organoclay is, in general, difficult to disperse in an organic medium to form the uniform gel structure which is required to thicken, or to increase the viscosity of, the organic medium. Various means have accordingly been used to improve the dispersibility of an organoclay in an organic medium, including the use of a polar organic material, such as a low molecular weight alcohol or ketone, as a dispersing aid, and the use of an excess of a specially selected organic cation in the preparation of the organoclay.

20 In Finlayson et al, U.S. Patent No. 4,105,578, an organophilic clay gellant having enhanced dispersibility in organic systems is disclosed which comprises the reaction product of a methyl benzyl dialkyl ammonium compound wherein the compound contains 20 to 35% alkyl groups having 16 carbon atoms, and 60 to 75% alkyl groups having 18 carbon atoms, and a smectite-type clay having a cation exchange capacity of at least 75 milliequivalents per 100 grams of said clay, and wherein the amount of said ammonium compound is from 100 to 120 milliequivalents per 100 grams of said clay, 100% active clay basis.

25 In Finlayson et al, U.S. Patent No. 4,412,018, an organophilic clay gellant and methods of using and making the same are disclosed, which comprises the reaction product of an organic cation, an organic anion and a smectite-type clay having a cation exchange capacity of at least 75 milliequivalents per 100 grams of said clay, such that an organic cation-organic anion complex is intercalated with the smectite-type clay and the cation exchange sites of the smectite-type clay are substituted with the organic cation. The examples of the patent illustrate the use of the organophilic clay in thixotropic unsaturated polyester compositions and in thixotropic coating compositions.

30 Unsaturated polyester compositions containing various gelling agents are well known. Additionally, it is known that in the preparation of glass fiber laminates of unsaturated polyester and the like, thixotropic gelling agents are used which allow for the ready mixing and spraying of these resins at high shear rates. At low shear rates, however, these gelling agents greatly increase the viscosity of the polyester, thus avoiding the drainage of the resin on vertical surfaces.

35 One of the most widely used gelling agents for unsaturated polyesters was asbestos fibers. Asbestos fibers assisted in producing thixotropic polyesters without significantly affecting resin clarity. However, in the past several years, it has become recognized that the use of asbestos under the usual manufacturing conditions is objectionable, because of its long-term adverse effects on health when inhaled. For this reason, the asbestos gelling agents were replaced by a silica aerogel. When about 1% of silica was dispersed in the resin, it provided effective thixotropy. However, such product is comparatively expensive, and because of low bulk density, presents storage and handling problems.

40 Consequently, the art has turned to the use of organoclays as gelling agents. Conventional organoclays cannot be dispersed in unsaturated polyester solution. They must be predispersed in monomer styrene and the gel subsequently blended with the polyester. This extra stage is expensive and inconvenient. It also limits the amount of organoclay that can be incorporated, to levels which can be physically handled in styrene: above about 8 wt % the gels become unmanageably stiff. Hence there is a need for organoclays which can be stirred directly into polyester solution, like fumed silica. This is demonstrated in the present invention.

Summary of the Invention

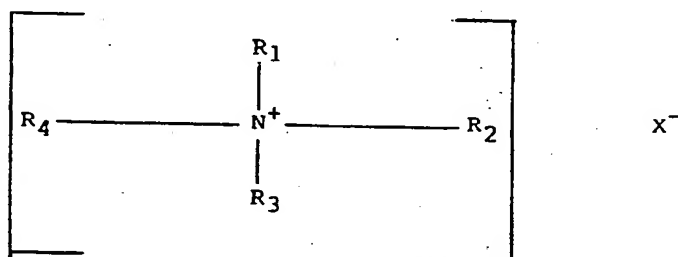
The organoclay employed in the present invention is prepared by a method described in U.S. Serial No. 765,259 filed August 13, 1985, which comprises the following steps:

- (a) A smectite clay is suspended in water to form a fluid suspension;
- (b) The aqueous suspension of the smectite clay is treated with a solution of an inorganic salt, the cation of which has a valency of at least two, the concentration of the salt being such as to flocculate the smectite clay substantially completely;
- (c) The suspension of the flocculated smectite clay is mixed with a quaternary ammonium compound at least one of the four alkyl groups of which has from 10 to 24 carbon atoms; and
- (d) The product of step (c) is dewatered.

In step (b) the valency of the cation is preferably 3, and most preferably the cation is aluminum. If the valency of the cation is 3 the concentration of the solution of the salt containing the cation is preferably in the range of 0.001 M to 0.02 M. If, however, the valency of the cation is 2 the concentration of the solution of the salt containing the cation must be greater and is preferably in the range from about 0.2 M to 2 M.

The suspension of the flocculated clay is preferably mixed with the quaternary ammonium compound in proportions such that there are present from 95 to 140 milliequivalents of quaternary ammonium cation per 100 g of dry clay.

In step (c) the aqueous suspension of the flocculated smectite clay is preferably mixed with molten quaternary ammonium compound. The quaternary ammonium compound preferably has the general formula:



wherein R_1 is a saturated or unsaturated alkyl group having from 10 to 24 carbon atoms, R_2 and R_3 , which may be the same or different, are each a saturated or unsaturated alkyl group having from 1 to 24 carbon atoms or an aralkyl group having from 7 to 10 carbon atoms, R_4 is an alkyl group having from 1 to 6 carbon atoms or an aralkyl group having from 7 to 10 carbon atoms, and X is OH, Cl, Br, NO_2 , CH_3SO_4 or CH_3COO .

Examples of such compounds are the benzyl methyl dialkyl ammonium chlorides, the dimethyl dialkyl ammonium chlorides, the benzyl dimethyl alkyl ammonium chlorides, the benzyl trialkyl ammonium chlorides and the methyl trialkyl ammonium chlorides, where the one or more alkyl group represents a mixture of hydrocarbon radicals derived from tallow having from 14 to 20 carbon atoms but in which C_{18} radicals preferably predominate (a typical analysis of such a mixture of hydrocarbon radicals contained in tallow is: C_{14} 2.0%; C_{15} 0.5%; C_{16} 19.0%; C_{17} 1.5%; C_{18} 66.0% and C_{20} 1.0%). The hydrocarbon radicals may be partially unsaturated as in natural tallow or may be substantially completely saturated as a result of treating the tallow with hydrogen in the presence of a suitable catalyst.

It has been found that these organoclays can readily be incorporated in resin compositions containing unsaturated polyester resins or epoxy resins.

These organoclays are self-dispersing products for unsaturated polyester/styrene systems and polar organic solvent systems.

By means of the present invention, there can be provided a novel thixotropic cross-linkable unsaturated polyester composition which has unique rheological properties, for example, an exceptionally high thixotropic index.

Detailed Description

The organophilic clays of this invention may be used without the need for a styrene pregel. In particular, polyester compositions may be prepared by mixing the organophilic clay with the final liquid polyester mixture prepared from a liquid unsaturated polyester and unsaturated aromatic monomer. The final

polyester compositions can then be cross-linked to produce coatings or glass fiber-reinforced laminates by methods well known in the art.

In a typical procedure the liquid unsaturated polyester resin is mixed in conventional apparatus with an unsaturated aromatic monomer to prepare a solution having a solids content between about 30 and 80% by weight polyester. The organophilic clays of the invention can then be added to the liquid laminating resin.

The unsaturated aromatic monomers of this invention are aromatic compounds to which is bonded one or more ethylenically unsaturated radicals such as a vinyl radical, substituted vinyl radical or an allylic radical. Suitable monomers include styrene, α -methyl styrene, divinyl benzene and allyl benzene. Styrene is preferred due to its effectiveness, wide use and availability. Such monomers are used in cross-linking the polyesters and also act as diluents to reduce viscosity.

The unsaturated polyesters useful in preparing the thixotropic compositions of this invention are polyesters of a dicarboxylic acid and a diol having a major amount of olefinic unsaturation, preferably 10 to 75 olefin groups per 100 ester groups. The olefinic unsaturation is preferably derived from the carboxylic acid although the diol may be unsaturated. Typical diols are ethylene glycol and propylene glycol. Typical unsaturated acids include maleic acid, fumaric acid. Anhydrides of these acids are also commonly used. Such polyesters are made by conventional techniques of esterification as well known in the art. Generally, polyesters having molecular weights of from about 400 to 10,000 and acid numbers in the range of from 0 to 50 mg KOH per gram of resin are useful for preparing the thixotropic composition of this invention.

The amounts of organophilic clay gellant used in polyester laminating resins can range from 0.25% to 10%, preferably 0.5 to 4%. Amounts larger than 10% may be employed but are not economical.

Practice of the present invention will now be illustrated by the following Examples, which however, are to be considered as merely illustrative of the invention, and not delimitive thereof.

The Hegman Gauge referred to in the following examples is used to determine the quality of the dispersion of solid particles in an organic liquid medium, and comprises a polished metal plate provided with a rectangular depression of tapering depth which varies uniformly from zero at one end to 100 μ m at the other end. A film of the organic liquid composition is spread evenly over the plate and a visual estimate of the coarsest particles present in the composition can be made.

If a substantial number of relatively coarse (10 - 100 micrometer) particles are present in the composition a definite "front" will be observed which, when compared with a scale provided alongside the depression, indicates the size of the largest particles present. If only a few particles in the above size range are present these will show up as specks in the depression and may be counted. The particulate solid material in a paint composition should be dispersed to such an extent that no front is visible when a sample of the paint is spread on a Hegman gauge and only a very small number, if any, specks can be seen.

Example I

Organoclay samples were prepared by the following method.

An aqueous suspension of bentonite was prepared by mixing raw Wyoming sodium bentonite in a blunger with sufficient water to form a suspension containing 10% by weight of dry clay. The suspension thus formed was passed through a No. 300 mesh British Standard sieve (nominal aperture 0.053 mm) and the undersize fraction was diluted to about 4% by weight of solids with water and subjected to a particle size separation in an intermittent discharge, continuous centrifuge at a flow rate of 1 litre per min. The fine fraction was then passed through a homogenizer as a pre-treatment to reduce particle size and increase uniformity. To a 500g sample of the homogenized fine fraction, enough water was added to make the organoclay reaction solids 2.3% by weight. To this was then added the calculated weight of aluminum chloride ($AlCl_3 \cdot 6H_2O$) which was required to give the desired concentration of aluminum chloride in the suspension. The suspension was then subjected to stirring by means of a paddle mixer for 15 minutes while the suspension was heated to a temperature of 65°C. There was then added to the heated suspension the calculated weight of a mixture of quaternary ammonium compounds and water isopropyl alcohol (in which form the quaternary ammonium compounds are available in commerce) which was required to give the desired loading of quaternary ammonium compounds on dry bentonite. The resultant mixture was then stirred in the paddle mixer for 30 minutes, filtered on a Buchner funnel, washed with hot water and dried for 1 1/2 hours at 60°C in a fluid bed drier. The dry product was then milled to the desired particle size.

The various organoclays were prepared according to the above procedure using a mixture of quaternary ammonium compounds comprising 75 mole% dimethyl benzyl hydrogenated tallow ammonium chloride (2MBHT) and 25 mole % dimethyl di(hydrogenated tallow) ammonium chloride (2M2HT), different concentrations of aluminum chloride being used in the preparation of the aqueous suspension of bentonite.

Each organoclay was milled to less than 0.250 mm. 1.5% by weight of each dry organoclay composition was incorporated into an unsaturated polyester resin composition using a laboratory stirrer rotating at 3,500 r.p.m. for 15 mins. The resin was a rapid-curing, general-purpose unsaturated polyester resin, marketed by the Scott Bader Company Limited under the trade name "CRYSTIC 196" (CRYSTIC is a Registered Trademark). It is believed to be a co-polymer of ortho-phthalic acid, fumaric acid and propylene glycol, having a number average molecular weight of about 3,000. Cobalt octoate accelerator was added at 0.01% by weight at the end of the mixing time. Crystic 196 as received from Scott Bader is a 70 percent by weight solution of polyester resin in styrene. This is diluted to 54 percent by weight polyester with extra styrene before use.

The viscosity of the polyester resin composition containing the organoclay as a gelling agent, was measured using a Brookfield RVT Viscometer at spindle speeds of 0.5 r.p.m., 5 r.p.m. and 50 r.p.m. The data are shown in Table 1. Thixotropic Index ratios are also given.

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$$\text{Thixotropic Index} = \frac{\text{viscosity in cp at 5 r.p.m.}}{\text{viscosity in cp at 50 r.p.m.}}$$

Table 1

Milli-Equivalents Quaternary Ammonium Compound per 100g clay	Concentration of Al ³⁺ ions in Aqueous Suspension M	Viscosity, cp			Thixotropic Index
		0.5 r.p.m.	5 r.p.m.	50 r.p.m.	
110	0	8400	1680	500	3.36
110	0.001	11600	2240	612	3.66
110	0.0025	15400	2760	596	3.97
110	0.005	4200	960	344	2.79
100	0.0025	17000	3000	724	4.14
105	0.0025	24000	4400	965	4.56
110	0.0025	15000	2880	708	4.07
115	0.0025	8200	1700	496	3.43
fumed silica at 1 wt %	-	17300	2944	645	4.56

Example II

Each organoclay, prepared as described in Example I, was milled to less than 0.080 mm and incorporated into component A of a Two-pack Epoxy Enamel.

This 19% pigment volume concentration white paint consists of 2 components, A and B. A is the base containing the epoxy resin; B is the polyamide curing agent solution. The ingredients are listed in their order of addition.

To prepare component A the following were mixed:

	<u>Ingredient</u>	<u>Description/Function</u>	<u>Supplier</u>	<u>Grams</u>
5	Epikote 1001-X-75	75 wt.% solution of epoxy resin in xylene	Shell Chemicals	157.0
10	Solvent mixture	65 wt.% Ethylene glycolmonoethyl ether acetate; 15 wt.% Methyl isobutyl Ketone 20 wt.% Xylene		47.5
15	Beetle 640	Urea formaldehyde resin, a flow control agent	British Industrial Plastics (BIP)	7.0
20	Nuosperse 657	Dispersant	Durham Raw Materials	3.5
25	Titanium Dioxide			149.0

The above ingredients were mixed in a water-cooled pot using a Cowles blade at 4,000 r.p.m. until a Hegman Gauge reading of $<10\mu\text{m}$ was obtained. The speed of the stirrer was reduced to 2,000 r.p.m. and the following added separately to the mix; the ingredients are listed in their order of addition:

	<u>Ingredient</u>	<u>Description/Function</u>	<u>Grams</u>
35	Solvent mixture	As above	42.5
	Organoclay		3.07

The stirrer speed was increased to 4,000 r.p.m. and the ingredients mixed for 30 minutes at which time a Hegman Gauge reading was taken.

Component B is separately prepared by mixing the following miscible ingredients.

	<u>Ingredient</u>	<u>Description/Function</u>	<u>Supplier</u>	<u>Grams</u>
45	Versamide 115	Polyamide liquid curing agent (amine value 210-220mg KOH/g)	Cray Valley Products	56.0
50	Xylene			35.0

Samples of the component A with organoclay and solvent were allowed to stand for 15 minutes and were then tested for viscosity at 21°C using a Brookfield RVT Viscometer at speeds of 1 r.p.m., 10 r.p.m., and 100 r.p.m.

A sample of the component A prepared in an identical manner but containing no organoclay was also tested for viscosity in the same way. Results are shown in Table 2.

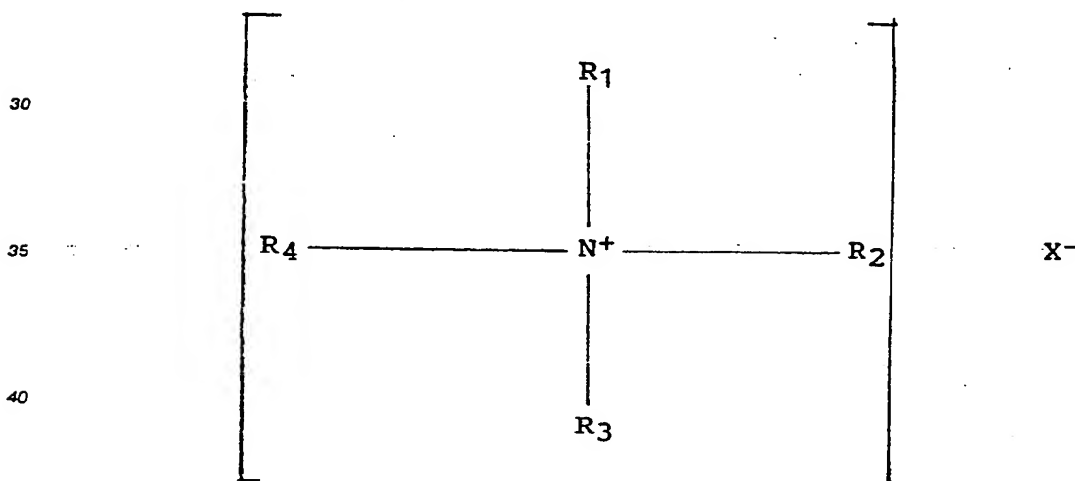
Table 2

Milli-Equivalents Quaternary Ammonium Compound per 100g clay	Concentration of Al ³⁺ ions in Aqueous Suspension M	Viscosity cp			Hegman Gauge Reading /cm
		0.5 r.p.m.	10 r.p.m.	100 r.p.m.	
110	0	21000 ²	3950	1060	+50
110	0.0025	28000	4750	1200	30
110	0.005	23000	4100	1040	10
100	0.0025	32000	5400	1460	30
105	0.0025	27000	4600	1310	20
No Organoclay		11000 ²	2200	660	10

It can be seen from the data in Example I and Table 1 that cross-linkable unsaturated polyester compositions having an unexpectedly high thixotropic index of above about 2.5, preferably above about 3.0 and more preferably at least about 4.0, can be obtained by means of the subject invention. It can also be seen from Example II that the organoclay is readily dispersible in a polar organic solvent system.

Claims

1. A resin composition comprising a resin chosen from an unsaturated polyester resin and an epoxy resin, and a readily dispersible organoclay, said organoclay being prepared by a method comprising the steps of:
 - (a) suspending a smectite clay in water to form an aqueous suspension;
 - (b) treating said aqueous suspension of the smectite clay with a solution of an inorganic salt, wherein the cation of said inorganic salt has a valency of at least 2, the concentration of the salt being such as to flocculate the smectite clay substantially completely;
 - (c) mixing the suspension of the flocculated smectite clay with a quaternary ammonium compound at least one of the four alkyl groups of which has from 10 to 24 carbon atoms; and
 - (d) dewatering the product of step (c).
2. A composition in accordance with Claim 1, wherein the valency of said cation is 3.
3. A composition in accordance with Claim 1 or 2, wherein said cation is aluminium.
4. A composition in accordance with Claim 1, 2 or 3, wherein the concentration of the solution of the salt containing the cation is in the range of from 0.001 M to 0.02 M.
5. A composition in accordance with any one of Claims 1 to 3, wherein the valency of said cation is 2, and wherein the concentration of the solution of the salt containing the cation is in the range of from about 0.2 M to 2M.
6. A composition according to any preceding claim, wherein the dewatered product of step (c) is dried and milled.
7. A composition according to any preceding claim, wherein the quaternary ammonium compound mixed with the aqueous suspension of the smectite clay is molten.
8. A composition according to any preceding claim, wherein the quaternary ammonium compound can be represented by the general formula:



- wherein R_1 is selected from saturated and unsaturated alkyl groups having from 10 to 24 carbon atoms, R_2 and R_3 , which may be the same or different, are each selected from saturated and unsaturated alkyl groups having from 1 to 24 carbon atoms and aralkyl groups having from 7 to 10 carbon atoms, R_4 is selected from alkyl groups having from 1 to 6 carbon atoms and aralkyl groups having from 7 to 10 carbon atoms, and x is selected from OH, Cl, Br, I, NO₂, CH₃SO₄ and CH₃COO.
9. A composition according to Claim 8, wherein the quaternary ammonium compound is chosen from benzyl methyl dialkyl ammonium chlorides, dimethyl dialkyl ammonium chlorides, benzyl dimethyl alkyl ammonium chlorides, benzyl trialkyl ammonium chlorides and methyl trialkyl ammonium chlorides in which the one or more alkyl group represents a mixture of hydrocarbon radicals derived from tallow having from 14 to 20 carbon atoms.
 10. A composition according to any preceding claim, wherein the smectite clay is mixed with the quaternary ammonium compound in proportions such that there are present from 95 to 140 milli-equivalents of quaternary ammonium cation per 100 g of dry clay.

11. A resin composition according to any preceding claim, in which the resin is an unsaturated polyester resin.

12. A resin composition according to any preceding claim, being a coating formulation.

13. A resin composition according to any preceding claim, in which the resin is used as an unsaturated polyester/styrene system.

14. An organoclay dispersed in a polar organic solvent system, useful in the preparation of resin compositions according to Claim 1, said organoclay being prepared by a method comprising the steps of:

(a) suspending a smectite clay in water to form an aqueous suspension;

(b) treating said aqueous suspension of the smectite clay with a solution of an inorganic salt wherein the cation of said inorganic salt has a valency of at least 2, the concentration of the salt being such as to flocculate the smectite clay substantially completely;

(c) mixing the suspension of the flocculated smectite clay with a quaternary ammonium compound at least one of the four alkyl groups of which has from 10 to 24 carbon atoms; and

(d) dewatering the product of step (c).

Claims for the following contracting States: AT, ES

1. A process for preparing a resin composition which process comprises combining a resin chosen from an unsaturated polyester resin and an epoxy resin with a readily dispersible organoclay, said organoclay having been prepared by a method comprising the steps of:

(a) suspending a smectite clay in water to form an aqueous suspension;

(b) treating said aqueous suspension of the smectite clay with a solution of an inorganic salt, wherein the cation of said inorganic salt has a valency of at least 2, the concentration of the salt being such as to flocculate the smectite clay substantially completely;

(c) mixing the suspension of the flocculated smectite clay with a quaternary ammonium compound at least one of the four alkyl groups of which has from 10 to 24 carbon atoms; and

(d) dewatering the product of step (c).

2. A process in accordance with Claim 1, wherein the valency of said cation is 3.

3. A process in accordance with Claim 1 or 2, wherein said cation is aluminium.

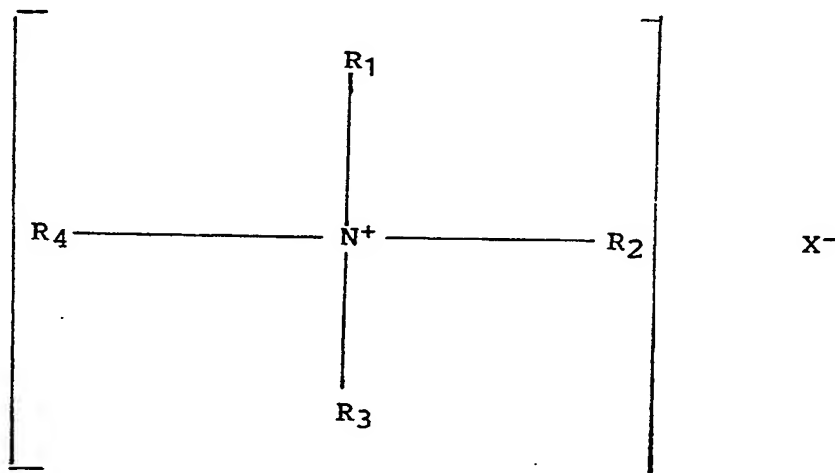
4. A process in accordance with Claim 1, 2 or 3, wherein the concentration of the solution of the salt containing the cation is in the range of from 0.001 M to 0.02 M.

5. A process in accordance with any one of Claims 1 to 3, wherein the valency of said cation is 2, and wherein the concentration of the solution of the salt containing the cation is in the range of from about 0.2 M to 2M.

6. A process according to any preceding claim, wherein the dewatered product of step (c) is dried and milled.

7. A process according to any preceding claim, wherein the quaternary ammonium compound mixed with the aqueous suspension of the smectite clay is molten.

8. A process according to any preceding claim, wherein the quaternary ammonium compound can be represented by the general formula:



wherein R₁ is selected from saturated and unsaturated alkyl groups having from 10 to 24 carbon atoms, R₂ and R₃, which may be the same or different, are each selected from saturated and unsaturated alkyl groups having from 1 to 24 carbon atoms and aralkyl groups having from 7 to 10 carbon atoms, R₄ is selected from alkyl groups having from 1 to 6 carbon atoms and aralkyl groups having from 7 to 10 carbon atoms, and X is selected from OH, Cl, Br, I, NO₂, CH₃SO₄ and CH₃COO.

9. A process according to Claim 8, wherein the quaternary ammonium compound is chosen from benzyl methyl dialkyl ammonium chlorides, dimethyl dialkyl ammonium chlorides, benzyl dimethyl alkyl ammonium chlorides, benzyl trialkyl ammonium chlorides and methyl trialkyl ammonium chlorides in which the one or more alkyl group represents a mixture of hydrocarbon radicals derived from tallow having from 14 to 20 carbon atoms.

10. A process according to any preceding claim, wherein the smectite clay is mixed with the quaternary ammonium compound in proportions such that there are present from 95 - 140 milli-equivalents of quaternary ammonium cation per 100 g of dry clay.

11. A process according to any preceding claim, in which the resin is an unsaturated polyester resin.

12. A process according to any preceding claim, being a coating formulation.

13. A resin process according to any preceding claim, in which the resin is used as an unsaturated polyester/styrene system.

14. A process which comprises dispersing an organoclay in a polar organic solvent, said organoclay having been prepared by a method comprising the steps of:

- (a) suspending a smectite clay in water to form an aqueous suspension;
- (b) treating said aqueous suspension of the smectite clay with a solution of an inorganic salt wherein the cation of said inorganic salt has a valency of at least 2, the concentration of the salt being such as to flocculate the smectite clay substantially completely;
- (c) mixing the suspension of the flocculated smectite clay with a quaternary ammonium compound at least one of the four alkyl groups of which has from 10 to 24 carbon atoms; and
- (d) dewatering the product of step (c).



European Patent
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EUROPEAN SEARCH REPORT

Application Number

EP 86 30 9796

DOCUMENTS CONSIDERED TO BE RELEVANT			
Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int. Cl. 4)
D,A	US-A-4 412 018 (FINLAYSON et al.) * Claims 1-24; column 26, lines 28-33 * ---	1,6-14	C 08 K 3/34 C 08 L 67/06
D,A	US-A-4 105 578 (FINLAYSON et al.) * Claims 1-5; column 3, lines 33-40 * ---	1,6-14	C 08 L 63/00 C 01 B 33/20
A	CHEMICAL ABSTRACTS, vol. 71, no. 22, 1st December 1969, page 325, abstract no. 105673r, Columbus, Ohio, US; N.K. MITRA et al.: "Flocculation characteristics of bentonite clay when substituted by different cations in exchangeable positions", & INDIAN CERAM. 1969 13(11), 257-61 * Whole abstract * -----	1-5	
			TECHNICAL FIELDS SEARCHED (Int. Cl.4)
			C 08 K C 01 B
The present search report has been drawn up for all claims			
Place of search THE HAGUE		Date of completion of the search 11-02-1988	Examiner DECOCKER L.
CATEGORY OF CITED DOCUMENTS			
X : particularly relevant if taken alone Y : particularly relevant if combined with another document of the same category A : technological background O : non-written disclosure P : intermediate document		T : theory or principle underlying the invention E : earlier patent document, but published on, or after the filing date D : document cited in the application L : document cited for other reasons ----- & : member of the same patent family, corresponding document	

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